

N 64 20632

Reprinted from *Experimental Mechanics*, March 1964

Technical Report No. 32-556

Some Low-modulus Birefringent Resins

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This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

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March 1964

Some Low-modulus Birefringent Resins

The formulation and casting techniques of some low-modulus polyurethane resins are discussed by the authors

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ABSTRACT—Information is given to enable the photoelastician to select and prepare his own clear, bubble-free, constant-thickness, low-modulus (500 psi or less) birefringent resins. Various urethane formulations are examined. The effects of environment, mixing, casting, molds, cure, post-cure and calibration are discussed. A procedure to select a particular formulation is suggested.

Introduction

The use of low-modulus birefringent coatings as a strain-measuring device has been successfully demonstrated for solid propellant.¹⁻³ Materials such as solid propellant require that a photoelastic coating have a modulus no greater than its own (less than 500 psi). It is also desirable that the Poisson's ratio of the coating be the same as that for the propellant (0.4 to 0.5). Magnitudes of propellant strains of interest may be of the order of 15 to 20 percent. The above studies have been restricted to coatings that did not exhibit viscoelasticity at ambient temperatures.

Studies done at JPL, as well as that which can be found in the literature, are presented in this paper as a current summary of the state of the art of low-modulus birefringent resins. It is assumed that a strain of 50 percent was an unrealistic propellant design criteria. Therefore, resins that did not exhibit four fringes at 50 percent strains were not considered in this study.

Birefringent resins with high elastic moduli are commercially available,⁴ but low-modulus resin sheets are difficult to obtain. The basic problems in the manufacture are mechanical in nature and are as follows:

1. Bubbles (entrapped gas or product gas) must be removed prior to curing or during curing.
2. A constant resin thickness must be maintained during curing.
3. The clearness of the resin is a function of the mold surface as well as the chemical composition, curing environment, etc.
4. Stability of the stress-optic and mechanical properties with time should be maintained.

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5. The chemical formulation should match the birefringent spectrum to the working strain level of the material under investigation.

One would expect that a linear proportional relationship exists between Young's modulus and optical sensitivity for a given resin family if a linear stress-strain optical response is exhibited. The empirical establishment of this relationship would then serve as a guide to the photoelastician in selecting a proper resin for a specific experiment.

Calibration of Resin Birefringence

The stress-optic law may be empirically defined for a linear elastic resin as

$$n_1 - n_2 = 2tC (\sigma_1 - \sigma_2) \quad (1)$$

or

$$n_1 - n_2 = 2tK (\epsilon_1 - \epsilon_2) \quad (2)$$

where

t = thickness of the resin, (in.)

C = stress-optic constant (actually drifts with strain), (psi)

σ_1, σ_2 = principal stresses, (psi)

$K = \frac{CE}{1 + \mu}$ = strain-optic constant (actually drifts with stress)

ϵ_1, ϵ_2 = principal strains, (in./in.)

μ = (Poisson's ratio)

E = Young's modulus, (psi)

In calibrating the resin, there is the problem of measuring $\sigma_1, \sigma_2 (=0)$, $t, n_1 - n_2$ and solving for C . This calibration can be readily obtained by use of a tensile machine, a camera (70 mm) to measure ϵ_1, ϵ_2 (grid displacements) on the resin, and Polaroid filters to observe $n_1 - n_2$ (colors). Knowing C, K can readily be computed by assuming that the relationships of stress and strain (valid for infinitesimal deformation) hold approximately for strains of the order of at least 30 percent. This round-about method is used to compute K instead of calibrating directly from eq (2) because ϵ_2 is not necessarily zero. Determination of ϵ_2 is difficult because of measurement inaccuracies. Because of the uncertainty of ϵ_2 at various regions in the tensile specimen, the assumption $\sigma_2 = 0$ is more useful in calibrating K through C . This is because μ may be taken as a

TABLE 1—CALIBRATION OF VARIOUS PROPERTIES OF HYSOL AS A RESULT OF CHANGING THE MIXING AND CURING PARAMETERS

Sample No.	Poisson's ratio at 15% strain	E, psi	$C \times 10^{-4}$, psi^{-1}	K	Shore A hardness	Cure environment; ^a time, hr/temperature, °C	Post-cure time in desiccator, days
Hysol 2085 = 100 gm/Hysol 3562 = 24 gm							
H-1	0.48	230	2.45	0.0039	48	G; 1.5/135 G; 3.5/100	21
H-1 ^c	0.48	490	2.00	0.0065	61	G; 1.5/135 G; 3.5/100	21
H-2	0.40	380	2.05	0.0054	55	H; 5/120	
H-2 ^c	0.48	640	2.00	0.0086	66	H; 5/120	
H-3	0.47	580	2.05	0.0082	63	G; 1.8/135 G; 4/100	
H-4	0.48	515	2.01	0.0068	61	G; 1.5/140 G; 4/100	16
H-5	0.40	530	2.05	0.0078	62	F; 5.6/RT F; 17/100	
Hysol 2085 = 100 gm/DB castor oil = 83 gm; mixed out of dry box							
H-6	0.45	20	8.60	0.0012	27	E; 1.5/130 E; 4/105	15
H-7	0.45	20	8.40	0.0012	27	G; 1.5/130 G; 4/105	31
H-8	0.44	20	8.00	0.0010	27	H; 1.5/135 H; 4/100	20
Hysol 4485							
H-9	0.47	1330	0.99	0.0085	64	^d	^d

^a E = sealed; F = nitrogen; G = vacuum; H = air.

^c Recalibrated 3 weeks later.

^d Sample purchased from manufacturer; conditions of cure, mold, and post-cure unknown.

constant throughout the resin. It is noted that the relationships defined from eqs (1) and (2) can be experimentally verified for strains of the order of 30 percent. The use of higher-order terms for strains and associated correction factors have not been found necessary for engineering analyses.

The strained birefringent resin may be thought of as an infinite array of uniaxial crystals with one optical axis normal to the surface. Schematically, each and every one of these crystals is experiencing a different strain (in a nonhomogeneous stress field), and correspondingly a different birefringence. Accepting this point of view, an excellent presentation of birefringence including a color-birefringent chart is found in Ref. 5. With such a chart, calibration or interpretation of birefringence for polychromatic light is simplified for engineering analysis.

Optical-mechanical Properties of Some Urethanes

The urethanes investigated all exhibited varying degrees of birefringence. Chemically, a urethane is the reaction product of an isocyanate with a hydroxyl. Urethane polymers can be prepared by reacting a diisocyanate (e.g., toluene diisocyanate, TDI) with a low-molecular-weight resin containing two or more hydroxyl groups per molecule. By suitable stoichiometry, a high-molecular-weight polymer is

obtained with repeating urethane linkages along the polymer chain.

Because isocyanates are basically toxic and react very readily with hydroxyl groups, the general practice has been to use a blocking technique. This technique involves the reaction of the isocyanate group with agents that form pre-polymers which are stable at room temperature, but which further react at the unreacted isocyanate sites at elevated temperatures.

An example of the blocking technique is Adiprene L-100, in which 2,4-toluene diisocyanate has been pre-reacted with 1,4-butylene oxide polyglycol to form a prepolymer. Theoretically, Adiprene L-100 can be cured to a cross-linked polymer by any compound with sufficient active hydrogens.

Diamines react with Adiprene to form a linear polymer where the resultant urea hydrogens continue the reaction. By varying the amount of diamine such as 4,4-methylene-bis-2-chloroaniline (MOCA) and the curing and mixing temperature, various moduli and elongations can be obtained.

Diols react slowly with Adiprene to yield linear, fusible polymers. Therefore, under the usual conditions, triols should be used to form a stable cross-linked urethane.

Hysol is a urethane very similar to Adiprene L-100 in composition and properties. Table 1 shows the optical-mechanical properties measured

TABLE 2—CALIBRATION OF VARIOUS PROPERTIES OF JPL-H URETHANES AS A RESULT OF CHANGING THE MIXING AND CURING PARAMETERS

Sample No.	Poisson's ratio at 15% strain	E, psi	$C \times 10^{-5}$, psi^{-1}	K	Shore A hardness	Cure environment; ^a time, hr/temperature, °C	Post-cure time in desiccator, days; ambient temperature
Estane = 94.28 gm; TDA = 1.57 gm; PPG = 13.23 gm							
JPL-H4	0.39	350	0.78	0.002	51	G; 70/110	21
JPL-H5	0.44	375	0.75	0.002	52	G; 18/120; 52/110	20
JPL-H6	0.42	160	1.35	0.001	49	G; 4/120; 65.5/110	21
JPL-H7	0.49	200	0.84	0.001	44	G; 19/104; 64/105	22
JPL-H9	0.47	260	0.66	0.001	42	G; 2.5/120; 68.5/110	20
JPL-H10	0.43	245	0.65	0.001	44	G; 4/116; 66/112	18
JPL-H12	0.42	205	1.40	0.002	52	F; 70/104	
JPL-H13	0.49	445	0.70	0.002	53	F; 70/104	
JPL-H14	0.41	250	0.60	0.001	47	F; 71/110	12
JPL-H15	0.47	250	0.58	0.001	42	G; 71/110	12
JPL-H19	0.42	200	0.56	0.0008	40	F; 22/RT; G; 51/110	14
Estane = 94.28 gm; TDA + PPG = 14.90 gm							
JPL-H16	0.44	240	0.51	0.0008	40	G; 72/110	9
JPL-H17	0.44	305	0.60	0.001	47	G; 72/107	9
JPL-H18	0.40	290	0.60	0.001	54	F; 72/RT; H; 51/105	7
Estane = 94.28 gm; TDA + PPG = 14.95 gm							
JPL-H8	0.45	320	0.65	0.001	47	G; 70/110	(F; 22) 19
Estane = 94.28 gm; TDA + PPG = 15.12 gm							
JPL-H11	0.48	450	0.69	0.002	53	G; 70/107	
Estane = 70.90 gm; TDA + PPG = 11.47 gm							
JPL-H20	0.43	270	0.56	0.010	47	G; 70/110	27

^a F = nitrogen; G = vacuum; H = air. Note: The PPG/TDA ratio was the same for all formulations.

at JPL for various Hysol formulations. These formulations consisted of those recommended by Hysol along with corresponding hybrids where the hardener (3562) was arbitrarily replaced with DB castor oil, a mixture of triols and diols. Calibration results show a good correlation between results reported in Refs. 6 and 7.

JPL-H is a urethane developed at JPL. It is prepared by reacting an Estane prepolymer with 2,4-toluene diamine (TDA) and Polyoxypropylene glycol (PPG) 2025 (available from Union Carbide Chemical Company as Niox Diol PPG 2025 elastomer grade) to form a resin which is cured at 100° C or 70 hours. The prepolymer Estane is commercially available from B. F. Goodrich Co. as Estane 5720X5. The formulations and properties of this resin are shown in Table 2 for various environments. Before use, 2,4-toluene diamine must be distilled, recrystallized and ground. To minimize contamination and exposure to atmospheric moisture, this resin was prepared in a dry box with a nitrogen atmosphere at a dew point below -20° F.

Resins were cast from Solithane 113 supplied by the Thiokol Chemical Corporation. Initially, tests were conducted on material cured with the curing agent supplied by Thiokol, such as Catalyst 300. By varying the ratio of the prepolymer (Solithane 113) to the amount of curing agent used (Catalyst 300), a wide variation of low-modulus materials can be made ranging from 50 to 500 psi at 100 percent strain (Table 3). Resins were also made replacing the curing agent with triols and DB castor oil.

Casting Techniques, Molds and Curing

Resin properties such as clarity, bubbles, modulus and birefringence are all dependent upon variation of composition, formulation, mixing, environment, casting, molds and curing schedule. The first two of these variables have been discussed. The last five variables and their interactions are now examined.

Environment

Since the isocyanate groups react readily with atmospheric moisture, the resins that showed the most promise were mixed in a moisture-free, inert atmosphere (dry nitrogen); resins were also mixed in an ambient environment for comparisons. To obtain a dry atmosphere, a leak-proof aluminum box can be constructed that can be purged with dry nitrogen. An indicating drierite may be used to indicate when any drying elements or desiccators need to be recharged. All materials (flasks, beakers, thermometers, etc.) may be dried by placing them in a hot (100° C) oven for 1 or 2 hours before transferring them to the dry box. Commercial resin components that arrive in containers sealed to exclude moisture may be transferred to the dry box under an N_2 blanket or otherwise opened within the dry box.

Mixing

The method that yielded the best results was found to be the use of a combination electric hot plate and

TABLE 3—CALIBRATION OF VARIOUS PROPERTIES OF SOLITHANE 113 AS A RESULT OF CHANGING MIXING PARAMETERS

Sample No.	Poisson's ratio at 15% strain	E, psi	$C \times 10^{-4}$, psi^{-1}	K	Shore A hardness	Additive; ^a pph Solithane 113	Cure environment; ^b time, hr/temperature, °C	Post-cure time in dessicator, days
S-1	0.43	535	2.25	0.0085	61	SA; 73.5	H; 1/150	..
S-2	0.46	600	2.35	0.0098	60	SA; 73.8	G; 1/150	..
S-3	0.48	560	2.40	0.0091	60	SA; 72.5	F; 1.25/125	12
S-3 ^c	0.45	600	2.30	0.0096	63	SA; 72.5	F; 1.25/125	12
S-4	0.48	675	2.20	0.0110	60	SA; 72.5	F; 2/RT; G; 0.5/115	12
S-5	0.43	455	2.30	0.0073	55	SA; 74.0	G; 1/150	..
S-6	0.41	430	2.60	0.0083	51	SA; 74.5	E; 4/150	..
S-7	0.49	460	2.30	0.0071	49	SB; 70.5	G; 1/140	..
S-7 ^c	0.46	660	2.20	0.0101	57	SB; 70.5	G; 1/140	..
S-8	0.48	150	2.55	0.0025	35	SB; 137.0	G; 0.75/150	6
S-8 ^c	0.46	155	2.35	0.0025	39	SB; 137.0	G; 0.75/150	29
S-9	0.45	165	2.45	0.0028	36	SB; 130.0	G; 1.25/125	7
S-9 ^c	0.48	170	2.50	0.0029	39	SB; 130.0	G; 1.25/125	24
S-10	0.47	175	2.40	0.0027	39	SB; 130.0	G; 1.25/110	7
S-10 ^c	0.48	190	2.40	0.0030	41	SB; 130.0	G; 1.25/110	24
S-11	0.47	145	2.95	0.0030	46	SB; 130.0	H; 1/RT; H; 1/130	7
S-11 ^c	0.48	190	2.25	0.0029	48	SB; 130.0	H; 1/RT; H; 1/130	24
S-12	0.41	40	1.60	0.0004	24	SC; 69.0	G; 4/150; G; 155/130	4
S-12 ^c	0.48	190	1.50	0.0020	44	SC; 69.0	G; 20/110	21
							G; 4/150; G; 155/130	
S-13	0.41	50	1.55	0.0006	26	SD; 67.5	G; 3.5/160; G; 16/115	5
S-13 ^c	0.45	245	1.55	0.0026	48	SD; 67.5	G; 3.5/160; G; 16/115	23
S-14	0.47	80	2.50	0.0012	21	SA; / 150.0	G; 1.5/150	9
S-15	0.46	500	2.25	0.0077	61	SA; / 73.7	G; 3/140	..
S-16	0.48	445	2.30	0.0067	53	SA; / 73.7	H; 3/140	..
S-17	0.44	30	9.20	0.0018	31	SB; / 140.5	E; 1/135	6
S-18	0.46	30	9.20	0.0018	31	SB; / 140.5	G; 1/135	6
S-19	0.47	35	8.80	0.0022	38	SB; / 134.0	H; 1/155	37
S-20	0.44	35	8.80	0.0022	54	SB; / 134.0	H; 2/RT; H; 16/60	36

^a SA = Solithane 300; SB = DB castor oil; SC = LHT-34 — one (Union Carbide); SD = Nixax Triol — LG 56 — one (Union Carbide).

^b E = sealed; F = nitrogen; G = vacuum; H = air; RT = room temperature.

^c Recalibrated 3 weeks later.

/ Mixed out of dry box.

magnetic stirrer. Using this method, the resin can easily be mixed in a vacuumized flask. The advantage of using a combination stirrer-hot plate is that the temperature of the mixture can be maintained or raised during the degassing or mixing period.

Casting

All casting was done in the nitrogen-atmosphere dry box. After thorough mixing (1 to 15 min), the vacuum was broken and the liquid elastomer was carefully poured into the mold within the dry box.

Molds

Various surfaces were investigated for resin adherence. Materials investigated were glass, brass, steel, Lucite, aluminum and Micarta along with various mold releases such as Teflon, etc. A mold consisting of two plates of aluminum, a lid and a base, with holes tapped through both plates to allow them to be bolted together, was considered satisfactory. Separation of these plates was insured by an aluminum circumferential gasket whose thickness was arbitrarily chosen. An O-ring groove was cut to

seal the mold. The surfaces that were to come in contact with the resin were made flat and parallel to each other and polished to a 4 to 10- μ in.-rms finish.

The important variable is the surface finish. No mold release is necessary (or desirable) for a high-surface finish (2–10 μ in. rms). Hence a clear, constant-thickness resin is obtained by positioning the above described mold in a vertical position during cure.

Curing Environment

The mold discussed above inherently satisfies the optimum condition (clearness) for resins containing diisocyanate, i.e., a cure environment which excludes moisture.

Post-curing

Initial calibrations of the polyurethane resins have shown that a post-cure is necessary to stabilize the resin properties. Optimum post-cure was found to be 14 days in a desiccator over Drierite for the JPL-H type polyurethane. This post-cure time has been found to be also about 14 days for most of the other urethane resins.

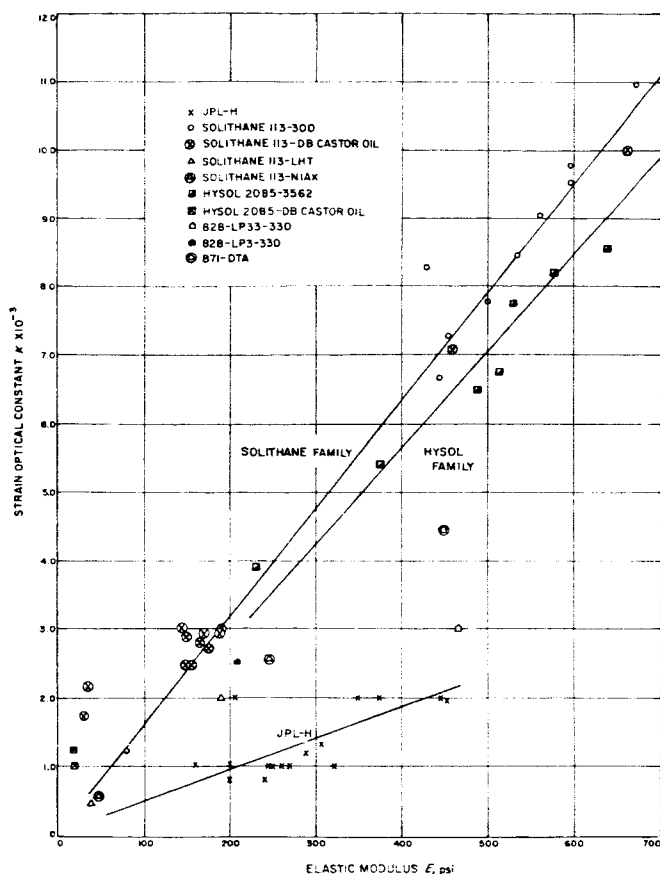


Fig. 1—Strain optical constant (K) of various low-modulus birefringent resins as a function of elastic modulus (E)

Low-modulus Urethane Selection

The photoelastician should choose a low-modulus birefringent resin that will exhibit an appropriate spectrum at the strain magnitude realm under investigation. It is desirable to avoid high-shear gradients. If polychromatic light is being used, the investigator will not want to exceed four fringes because of "color wash-out." In general, an attempt to make respectable measurements will require that various resins of different sensitivities be used simultaneously. One resin is suited to, say, 7 percent strains and another at 20 percent strains. The point to be made is that there is no one family of resins that may be considered universal. A certain amount of leeway is afforded by thickness changes. However, new errors are introduced by having either too thin or too thick a coating.

The urethane resins may also be used to make at least 200 cu. in. models. Molds for such models should be constructed in the manner described above for flat molds.

Should the photoelastician require an extremely low modulus (50 to 100 psi), it is suggested that the resin be calibrated a day or so after cure, just prior to a strain measurement. Calibration of a sample coupon just after an experiment should be performed to insure that the physical properties have not

changed significantly during the experiment.

Figure 1 illustrates the linear relationship between Young's modulus E , and the strain-optical constant K for various resin formulations. This linear relationship was predictable from strain-optic theory. The usefulness of such a relationship to the photoelastician is that any desired strain-optic constant may be ordered from a resin manufacturer by simply ordering a resin of a known formulation with some specific modulus. Note that resin manufacturers are accustomed to publishing only the modulus of various formulations as a description of their physical properties.

Summary

1. Sufficient data have been gathered to enable the photoelastician to prepare a clear, bubble-free, constant-thickness, low-modulus (500 psi or less) birefringent resin.

2. The choice of a low-modulus birefringent resin is dependent upon the various requirements, e.g., if polychromatic light is used, it is desirable that four fringe orders be observed at the strain magnitude of greatest interest.

3. A strained resin coating may be thought of as an infinite array of uniaxial crystals whose optic axis is normal to the surface.

4. Solithane resin was found to have the greatest birefringence, lowest modulus, and greatest ease of manufacture.

5. Criteria to resin manufacture are based on a dry environment, degassing during mix, a mold surface finish of the order of 2 to 10 μ in. rms, moisture-free curing, and post curing.

6. Figure 1 illustrates the linear relationship that exists between the strain-optical constant K and the elastic modulus E for a given resin family. Such information may be used in selecting a resin to meet a given experiment.

Acknowledgments

The investigation in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, under Advanced Research Projects Agency Letter Order No. 107-60, and National Aeronautics and Space Administration Contract NAS-7-100.

Bibliography

1. San Miguel, A., "Propellant Strain Analysis by the Photoelastic Coating Technique," *Bulletin of the Twentieth Meeting, JANAF Solid Propellant Information Agency, The Johns Hopkins University, Silver Spring, Md., November 1961.*
2. San Miguel, A., "Strain Measurements of a Pressurized Solid Propellant Grain," *Technical Report No. 32-182, Jet Propulsion Laboratory, Pasadena, Calif., March 15, 1962.*
3. San Miguel, A., "An Experimental Method to Measure the Strain Energy Function W ," *Technical Report No. 32-365 Jet Propulsion Laboratory, Pasadena, Calif., December 20, 1962.*
4. McMaster, R. C. (Editor), "Photoelastic-Coating Tests," *Nondestructive Testing Handbook, Vol. II, Ronald Press, New York, N. Y., 1959.*
5. Bloss, F. D., *An Introduction to the Methods of Optical Crystallography*, Holt, Reinhart & Winston, Inc., New York, N. Y., 1961.
6. "Flexible Photoelastic Casting Resin," *Bulletin E-105, Hysol Corp., Olean, N. Y., April 1951.*
7. Dally, J. W., Riley, W. F., and Durelli, A. J., "A Photoelastic Approach to Transient Stress Problems Employing Low-Modulus Materials," *Journal of Applied Mechanics, December 1959.*